

## SHAPE-SELECTIVE CATALYSIS IN ZEOLITES

Sigmund M. Csicsery

Chevron Research Company, Richmond, California 94802

### Introduction

Zeolites have four properties that make them especially interesting for heterogeneous catalysis: (1) they have exchangeable cations, allowing the introduction of cations with various catalytic properties; (2) if these cationic sites are exchanged to  $H^+$ , they can have a very high number of very strong acid sites; (3) their pore diameters are less than 10 Å; and (4) they have pores with one or more discreet sizes. These last two account for their molecular sieving properties. Zeolites have been applied as catalysts since 1960.

Pore diameters in molecular sieves depend on the number of tetrahedra in a ring (Figure 1). The actual pore size also depends on the type of cation present. Molecules like ammonia, hydrogen, oxygen, and argon can go through the pores of practically every type of molecular sieve. Type "A" sieves have cubic structure with pores just about big enough to allow normal paraffins through. Cations, however, occupy positions which block part of the pores. Monovalent cations (e.g., sodium, potassium) restrict the pore size to below ~4 Å. None of the organic molecules (except methane) would be able to penetrate NaA, or LiA zeolites. Divalent cations, however, occupy only every other cationic position leaving enough space for normal paraffins to diffuse through. Isobutane is slightly wider than the pores of CaA so cannot enter. However, molecules with nominal dimensions of perhaps half an angstrom too large can make their ways through narrower pores than expected because molecular vibration allows them to wiggle through. In addition, bond cleavage, followed by reconstruction of the broken bond, could facilitate the diffusion of larger molecules through narrow pores (1).

If almost all of the catalytic sites are confined within this pore structure and if the pores are small, the fate of reactant molecules and the probability of forming product molecules are determined mostly by molecular dimensions and configurations. Only molecules whose dimensions are less than a critical size can enter the pores, have access to internal catalytic sites, and react there. Furthermore, only molecules that can leave appear in the final product.

### Types of Shape Selectivities

We can distinguish various types of shape selectivities, depending on whether pore size limits the entrance of the reacting molecule, or the departure of the product molecule, or the formation of certain transition states.

Reactant selectivity occurs when only part of the reactant molecules are small enough to diffuse through the catalyst pores (Figure 2).

Product selectivity occurs when some of the product formed within the pores are too bulky to diffuse out as observed products. They are either converted to less bulky molecules (e.g., by equilibration) or eventually deactivate the catalyst by blocking the pores (Figure 2).

Restricted transition state selectivity occurs when certain reactions are prevented because the corresponding transition state would require more space than available in the cavities. Neither reactant nor potential product molecules are prevented from diffusing through the pores. Reactions requiring smaller transition states proceed unhindered.

Molecular traffic control may occur in zeolites with more than one type of pore system. Reactant molecules here may preferentially enter the catalyst through one of the pore systems while products diffuse out by the other. Counter-diffusion is, thus, minimized here.

Examples will be discussed for each type of shape selectivity.

### Diffusion

The importance of diffusion in shape-selective catalysis cannot be overemphasized. In general, one type of molecule will react preferentially and selectively in a shape-selective catalyst if its diffusivity is at least one or two orders of magnitude higher than that of competing molecular types (2-5). Too-large molecules will be absolutely unable to diffuse through the pores. Even those molecules which react preferentially have much smaller diffusivities in shape-selective catalysts than in large-pore catalysts.

### Reactant- and Product-Type Shape Selectivities

Shape selectivity was first described by Weisz and Frillette in 1960. P. B. Weisz, N. Y. Chen, V. J. Frillette, and J. N. Miale were not only the pioneers of shape-selective catalysis; but in their subsequent publications they demonstrated its many possible applications. They have described many examples of reactant- (and product-) type shape selectivity. Examples are selective hydrogenation of n-olefins over CaA-type (6-7) and Pt ZSM-5 (8) molecular sieves (Figure 4).

Most applications and manifestations of shape-selective catalysis involve acid-catalyzed reactions such as isomerization, cracking, dehydration, etc. Acid-catalyzed reactivities of primary, secondary, and tertiary carbon atoms differ. Tertiary carbon atoms react inherently much easier than secondary carbon atoms. Primary carbon atoms don't form carbonium ions under ordinary conditions and therefore do not react. Therefore, in most cases isoparaffins crack and isomerize much faster than normal paraffins. This order is reversed in most shape-selective acid catalysis; that is, normal paraffins react faster than branched ones which sometimes do not react at all.

### Restricted Transition State-Type Selectivity

In restricted transition state-type selectivity, certain reactions are prevented because the transition state is too large for the cavities of the molecular sieve. An example is acid-catalyzed transalkylation of dialkylbenzenes (9) (Figure 3). In this reaction one of the alkyl groups is transferred from one molecule to another. This is a bimolecular reaction involving a diphenylmethane transition state.

Meta-xylene in this reaction will yield 1,3,5-trialkylbenzene. Mordenite does not have enough space for the corresponding transition state. Thus, whereas the 1,2,4-isomer can form, the 1,3,5-isomer cannot (10,11). Symmetrical trialkylbenzenes are absent from the product, although they are the predominant components of the trialkylbenzene isomer mixtures at equilibrium (12-13). Figure 5 shows product distributions over Zeolon H-mordenite. Isomerization rates of the symmetrical mesitylene and the smaller hemimellitene over mordenite and HY are almost identical. This shows that symmetrical trialkylbenzenes are themselves not hindered within the pores of H-mordenite. In isomerization, the transition state involves only one molecule; so there is enough space to form the transition state in the internal cavity of the sieve.

Another example for transition state-type selectivity is isobutane isomerization over HZSM-5 (14-16).

One can distinguish experimentally between reactant and product-type selectivities and restricted transition state-type selectivities by studying particle size effects. Observed rates depend on the intrinsic, uninhibited rate constant and, if mass transfer is limiting, on the diffusivities of the reactant (or product) molecules and on the catalyst particle size. Reactant and product selectivities are mass transfer limited and, therefore, affected by crystallite size whereas restricted transition-state selectivity is not. Haag, Lago, and Weisz used this method to determine the causes of shape selectivity in the cracking of  $C_6$  and  $C_9$  paraffins and olefins over HZSM-5 (17).

The crystallite size effects observed allowed Haag, Lago, and Weisz to calculate effective diffusivities. This was the first known case for determination of molecular diffusivities in a zeolite at steady state and actual reaction conditions (Figure 6). Diffusivities decrease by four orders of magnitude from normal to gem-dimethyl paraffins. While branching has a large effect, the influence of the length of the molecule is small. Olefins have similar diffusivities to the corresponding paraffins. One surprising observation is that these diffusivities are about an order higher than the calculated Knudsen diffusivities.

An important consequence of the lack of space for the bulky transition state for transalkylation within HZSM-5 is that xylene isomerization proceeds without trimethylbenzene formation. This improves xylene yields and increases catalyst life.

The most important example of restricted transition state-type selectivity is the absence (or near absence) of coking in ZSM-5 type

molecular sieves. This has great significance because certain reactions can occur in the absence of metal hydrogenation components and high hydrogen pressure. Coking is less severe in ZSM-5 because the pores lack enough space for the polymerization of coke precursors. On ZSM-5 the coke is deposited on the outer surface of the crystallites, whereas in offretite and mordenite most of the coke forms within the pores (18) (Figure 7). Activity is barely affected in the first case, while it decreases rapidly in the second.

In large pore zeolites (e.g., HY, mordenite) the most significant step in coking is probably the alkylation of aromatics (19-22). These alkylaromatics cyclize or condense into fused-ring polycyclics, which eventually dehydrogenate to coke. Paraffins could also contribute to coking via conjunct polymerization, which leads to naphthenes.

### Molecular Traffic Control

Molecular traffic control is a special type of shape selectivity. It could occur in zeolites with more than one type of intersecting pore systems. Reactant molecules here may preferentially enter the catalyst through one of the pore systems while the products diffuse out of the other. This may minimize counterdiffusion and, thus, increase reaction rate (23-24).

ZSM-5 has two types of channels, both of which have ten-membered ring openings. One channel system is sinusoidal and has nearly circular (5.4 Å x 5.6 Å) cross-section. The other channel system has elliptical openings (5.2 Å x 5.8 Å). These are straight and perpendicular to the first system (25-26). Whereas linear molecules can occupy both channel systems, 3-methylpentane and p-xylene occupy only the linear, elliptical pores. These suggest that normal aliphatics can diffuse freely in both systems; but aromatics and isoparaffins prefer the linear, elliptical channels. Examples might be benzene alkylation with ethylene, and toluene alkylation with methanol over ZSM-5 catalysts (27).

In "reverse molecular traffic control" small product molecules diffuse out through pores too narrow for larger reactants, thus avoiding counterdiffusion (28). Examples might be catalytic dewaxing or xylene isomerization (27).

Sequential adsorption measurements did not support the concept of molecular traffic control (29). However, it is questionable whether such kinetic phenomena can be proven or disproven by adsorption measurements (30).

Product selectivity, restricted transition state-type selectivity, and molecular traffic control may all contribute to several reactions in which p-xylene is formed above its equilibrium concentrations over ZSM-5 zeolite (2,4,5,31,32,33).

### Control of Shape Selectivity

Shape selectivity can be improved by reducing the number of active sites on the external surface of zeolite crystallites. The external surface of a molecular sieve can be neutralized by poisoning with a

large molecule (34). The extent of shape selectivity can be also controlled by cations (35-38). Decreasing the aluminum content in the last stage of crystallization of ZSM-5 zeolites is another way to reduce the number of active sites on the outside surface of crystallites (39) and, thus, improve shape selectivity.

### Erionite

Erionite (41-42) can selectively distinguish between normal and isoparaffins. Over erionite the otherwise much-more-reactive 2-methylpentane reacts 50 times slower at 430°C than normal hexane at 320°C. The cavity of erionite has dimensions similar to the length of n-octane. This coincidence is responsible for the so-called "cage" or "window" effect (42-46).

### Quantitative Measure of Shape Selectivity

A quantitative measure of shape selectivity (called "constraint index") compares the cracking rates of normal-hexane and 3-methylpentane (46) (Figure 37). Silica-alumina has a constraint index of 0.6. This ratio represents the intrinsic cracking rates of normal paraffins and isoparaffins. Mordenite and rare earth Y are similarly unselective. Erionite has a very high "constraint index," and so do various ZSM catalysts.

### Applications

We could remove undesirable impurities by cracking them to easily removable molecules and distilling them away [such as in Selectoforming (47, 48) and catalytic dewaxing (49-52)]. Impurities can also be selectively burned inside molecular sieves and removed as CO<sub>2</sub> and CO. Or impurities can be converted to harmless molecules.

One important class of applications of shape selectivity is to avoid undesirable reactions. For instance, in xylene isomerization transition state-type selectivity limits transalkylation and coking over ZSM-5 sieve (53). In toluene alkylation or disproportionation reactions leading to the undesirable isomers (o- and m-xylenes) are avoided (52-53). Most of these applications will be discussed in detail by subsequent speakers of this Symposium.

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FIGURE 1  
PORE DIAMETERS IN ZEOLITES

No. of Tetrahedra in Ring	Maximum Free Dia., Å	Example
6	2.8	
8	4.3	Erionite, A
10	6.3	ZSM-5, Ferrierite
12	8.0	L, Y, Mordenite
18	15	Not Yet Observed

Typical Hydrocarbon Dimensions:

Benzene =  $5.7 \text{ Å} \times 2.2 \text{ Å}$

n-Hexane =  $3.5 \times 4.2 \text{ Å}$

FIGURE 2

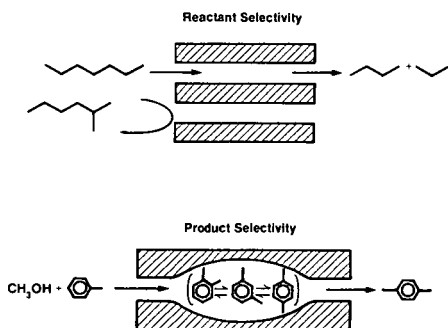
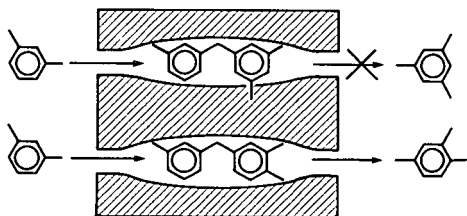


FIGURE 3

RESTRICTED TRANSITION STATE SELECTIVITY

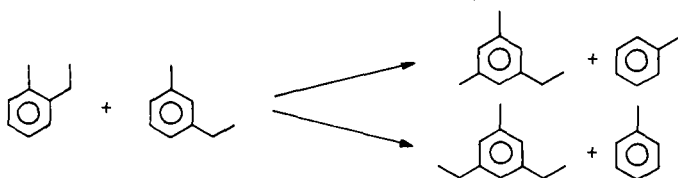


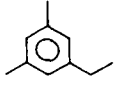
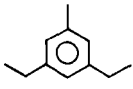
# **FIGURE 4** **SHAPE SELECTIVE HYDROGENATION** **OVER Pt - ZSM-5**

<u>Catalyst</u>	<u>Temp., °C</u>	<u>Pt - Al<sub>2</sub>O<sub>3</sub></u>	<u>Pt - ZSM-5</u>
<b>Hydrogenated, %</b>			
<b>Hexene</b>	<b>275</b>	<b>27</b>	<b>90</b>
<b>4,4-Dimethylhexene-1</b>	<b>275</b>	<b>35</b>	<b>&lt;1</b>
<b>Styrene</b>	<b>400</b>	<b>57</b>	<b>50</b>
<b>2-Methylstyrene</b>	<b>400</b>	<b>58</b>	<b>&lt;2</b>

Dessau, J. Catal., 77, 304 (1982).

FIGURE 5  
RESTRICTED TRANSITION STATE-TYPE SELECTIVITY IN THE  
TRANSALKYLATED PRODUCT DISTRIBUTION OF  
METHYLETHYLBENZENE



<u>Catalyst</u>	<u>Reaction Temperature, °C</u>	 % of Total C <sub>10</sub>	 % of Total C <sub>11</sub>
H-Mordenite	204	0.4	0.2
HY	204	31.3	16.1
Silica-Alumina	315	30.6	19.6
Thermodynamic Equilibrium	315	46.8	33.7

Csicsery, J. Catal. 19, 394 (1970).

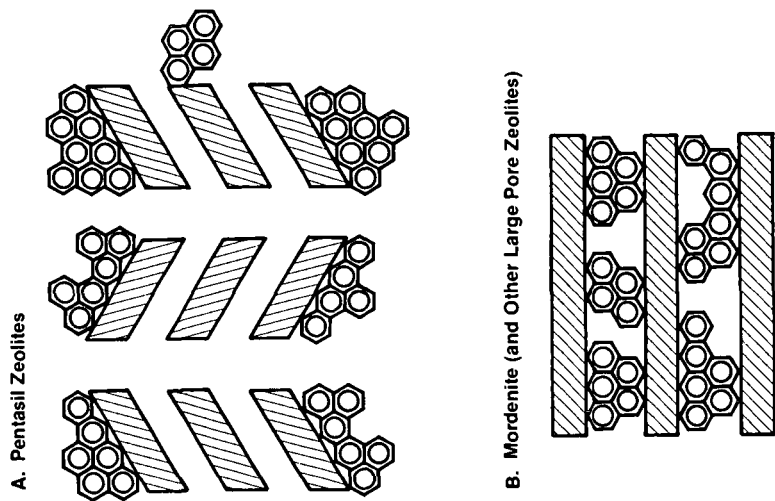
**FIGURE 6**  
**DIFFUSIVITIES IN ZSM-5**  
**538°C**

Structure	D at 538°C, cm <sup>2</sup> /S
<chem>C-C-C-C-C=C</chem>	$3 \times 10^{-4}$
<chem>C-C-C-C=C-C</chem>	$4 \times 10^{-5}$
<chem>C-C-C-C-C</chem>	$2 \times 10^{-8}$
<chem>C-C-C-C=C</chem>	$7 \times 10^{-8}$
<chem>C-C-C-C-C-C</chem>	$3 \times 10^{-8}$

Haag, Lago, and Weisz, Faraday General Discussions, 72, 317 (1982).

**FIGURE 7**

**COKE FORMATION IN ZEOLITES**



Dejaifve, et al., J. Catal., 70, 123 (1981).

# EXTENDED ABSTRACT

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## CATALYTIC, PHYSICAL AND ACIDIC PROPERTIES OF PENTASIL ZEOLITES

Jacques C. Védrine

Institut de Recherches sur la Catalyse, C.N.R.S.,  
2, av. Albert Einstein F 69626 Villeurbanne FRANCE

A large amount of efforts has been done in the recent years to understand the fascinating shape selective properties of ZSM-5 or ZSM-11 zeolites<sup>(1-4)</sup>. It has appeared that the acid strength of the Brönsted sites varies in a wide range for a same sample<sup>(5)</sup>. Moreover, depending on preparation conditions, the morphology and size of the zeolitic crystallites and the Al concentration within a crystallite and between crystallites may vary drastically<sup>(6-7)</sup>. It follows that it is somewhat difficult to rationalize the effects of particle size, of acid strength and of the nature of the zeolite (-5 or -11) on the catalytic properties of the catalyst for acid-type reactions like methanol conversion or alkylation of aromatics. The purpose of this presentation is to sum up some of our recent works in that field.

Experimental part : ZSM-5 and ZSM-11 samples have been prepared in the laboratory following the procedures described in ref. 8 and 9 respectively. For ZSM-5 samples the Al content of the samples was varied by using different Al concentration in the preparation mixture. For ZSM-11 samples the temperature and duration of the preparation were chosen to be 100°C, one month (sample 1) and 170°C, one week (samples 2 and 3). Chemical compositions were determined from atomic absorption measurements and are given in table 1. The samples were calcined under N<sub>2</sub> flow at 500°C and then at 540°C under air flow. Acidification was performed by exchanging Na cations by NH<sub>4</sub><sup>+</sup> in aqueous solution M/2 at 80°C, and by deammoniation at 540°C under air flow. One ZSM-5 sample was treated by a trimethylphosphite solution in n-octane at 120°C as described in ref. 10 resulting in a so called P-ZSM-5.

Table 1 : Physical characteristics of the different samples

Samples zeolite type modification	1 ZSM-11 no	2 ZSM-11 no	3 ZSM-11 no	4 ZSM-5 no	5 ZSM-5 no	6 P-ZSM-5 Phosphorus (1.1 wt%)
<u>Chemical analysis</u> atoms : Si : Al Na : (Si+Al)×10 <sup>2</sup>	37 0.3	31 0.5	43 0.1	23 0.2	9 0.7	10 0.7
<u>XPS data</u> atoms : Si : Al	24	30	70	26	10	9
<u>TEM analysis</u> Size of grains(μm) shape	0.6 <sup>+</sup> 0.2 aggre- gate  spheroi- dal	1-2 core + needles  spheru- litic	6 <sup>+</sup> 2 core + need- les spheru- litic	0.5-2 paralle- pipeds	0.5-2 paralle- pipeds	0.5-2 paralle- pipeds

Catalytic experiments were carried out in a flow microreactor (100 mg of catalyst) and analyses were performed on stream by gas chromatography.

Acidity characterization was performed using infra-red spectroscopy and micro-calorimetry of  $\text{NH}_3$  adsorption at  $150^\circ\text{C}$ . The morphology of the zeolite grains was determined using a high resolution transmission electron microscope JEOL 100 CX and Al distribution within the grain was determined with a high resolution EDX-STEM from Vacuum Generators (HB 5). Surface composition of the grains was measured by XPS using a monochromatized HP 5950 A spectrometer. X ray diffraction patterns were obtained using a conventional  $\text{CuK}\alpha$  X ray source. At last the capacity of n-hexane absorption at room temperature was measured by volumetry.

### Experimental results

The crystallinity of the samples prepared in the laboratory was determined by X ray diffraction, infra-red spectroscopy of the vibrational modes ( $550 : 450 \text{ cm}^{-1}$  ratios)<sup>(11)</sup>, high resolution electron microdiffraction and absorption capacity for n-hexane (11-12 wt %). All samples were found to be well crystallized materials except sample 1 which probably contained approximately 30 % of amorphous silica<sup>(10)</sup> and 70 % of aggregates of tiny crystallites (5-10 nm in size) as evidenced from i.r. and n-hexane absorption data. The other two ZSM-11 samples (samples 2 and 3) were formed of a core constituted by an aggregate of small 5-10 nm crystallites and of needles (500-1000 nm in size) emerging from the core with a spherulitic shape<sup>(7)</sup>. High resolution microdiffraction unambiguously showed that the tiny crystallites were well crystallized ZSM zeolite. ZSM-5 samples were formed of well crystallized parallelipeds of 0.5 to 2  $\mu\text{m}$  in size. Physical and chemical characteristics of the samples are given in table 1. Their catalytic properties for methanol conversion and alkylation of toluene by methanol are summarized in tables 2 and 3.

Table 2 : Catalytic properties of ZSM-5 and ZSM-11 samples in the reaction of methanol conversion at  $370^\circ\text{C}$  with  $\text{N}_2$  as a carrier gas, flow rate =  $5 \text{ l h}^{-1}$ , WHSV =  $11 \text{ h}^{-1}$

Samples	1	2	3	4	5	6
Conversion (%)	90	84	70	89	89	89
<hr/>						
<u>Hydrocarbons %</u>						
aliphatics	80	84	75	78	70	84
aromatics	20	16	25	22	30	16
<hr/>						
<u>Aromatics (%)</u>						
xylenes	26	27	29	46	50	64
$\text{A}_6 + \text{A}_7$	6	7	5	9	6	8
Others	68	66	66	45	44	28
(m + p) : O xylenes	3	3	5	13	11	35

**Table 3** : Catalytic properties of ZSM-5 and ZSM-11 samples in the reaction of alkylation of toluene by methanol at 400°C, with N<sub>2</sub> as a gas carrier and a total flow rate equal to 1.85 l h<sup>-1</sup>, WHSV = 4.5/5 h<sup>-1</sup>

Samples Zeolite	2 ZSM-11	4 ZSM-5	5 P-ZSM-5
Conversion (%)			
methanol	100	98	100
toluene	18	16	10
Hydrocarbons (%)			
aliphatics	1.3	4.1	11.6
xylene	81.0	88.0	84.5
trimethylbenzenes	12.9	4.1	1.0
others	4.8	3.8	4.9
Selectivities (%)			
p-xylene	29.1	52.1	94.6
m-xylene	49.8	36.5	3.8
o-xylene	21.1	11.4	1.4
TMB 135	2.3	-	-
TMB 124	94.6	100	100
TMB 123	2.3	-	-

The main features of catalytic properties are that ZSM-5 samples present more shape selective properties than ZSM-11 whatever the particle size, presumably because ZSM-11 has more free space (+ 30 %) at the channel intersections. Detailed analysis of the methanol conversion reaction<sup>(7)</sup> shows that when the grain size of ZSM-11 samples increases more light hydrocarbons (C<sub>1</sub> + C<sub>2</sub>) and less heavier hydrocarbons (C<sub>6</sub><sup>+</sup> and A<sub>9</sub>) are formed. This very probably arises from the longer length path for the reactants when the particle size increases.

The i.r. OH bands at 3720-3740 and 3600-3605 cm<sup>-1</sup> were observed for all samples. The 3600 cm<sup>-1</sup> band was shown by NH<sub>3</sub> adsorption to be acidic while the 3720-3740 cm<sup>-1</sup> band was shown to have its relative intensity decreasing when the particle size increased due to a decrease in the number of terminal silanols. Modification by phosphorus was shown to decrease the number of OH groups by about one half but their strength remained comparable<sup>(10)</sup>. The EDX-STEM characterization showed that Al was not homogeneously localized in the zeolite framework. For spherulitic ZSM-11 grains the needles were shown to present in average about twice less Al than the core and even more an heterogeneous distribution of Al from the inner to the outer layers. For ZSM-5 samples heterogeneity in Al concentration within a same zeolitic grain or between grains was observed which precluded any rationalized law<sup>(7)</sup>.

Acidity strength and acid site concentration were determined by measuring microcalorimetrically the differential heat of ammonia adsorption at 150°C. It was observed that the strongest acid sites were obtained for relatively low Al content but obviously the number of strong acid sites decreased with the Al content decreasing. Acidity strength was observed to be heterogeneous which is in agreement with the heterogeneity in Al distribution. The number of strong acid sites was found to equal 1.6, 1.8, 1.8, 2.4, 2.3, 1.3 per u.c respectively for samples 1 to 6, after outgassing at 400°C.

Conclusions : These characterizations lead to the following conclusions :

- . Crystal growth of ZSM-11 particles seems to be particularly difficult leading to aggregates or core of tiny crystallites, 5-10 nm in size with a relatively high Al content (Si : Al  $\approx$  30 against 50 in the preparation mixture). When Al content is low the crystal growth is then sharply enhanced
- . ZSM-5 presents much more shape selectivity for less bulky aromatics than ZSM-11 in methanol conversion and toluene alkylation reactions. This is presumably due to larger free space at the channel intersections of ZSM-11 sample.
- . Acid strength and site distributions do not seem to play an important role in selectivity for the previous reactions as far as acid sites of sufficient strength are present.
- . The particle size which modifies the channel length plays only a secondary role in the selectivity for aliphatics and aromatics.
- . The preparation conditions particularly Al concentration and stirring during synthesis seem to play a great role in the crystal growth and in the morphology of the zeolitic grains.

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